

even in the presence of a heterogeneous catalyst.

In this example the estimation of Δv^\ddagger was very crude, so to speak only qualitative. Frequently, this factor can be calculated with sufficient accuracy. Thus, the comparison between experimental and theoretical results (as obtained from equation (2)) enables one to decide on the validity of a certain activated complex model. Let us apply this principle for two diene syntheses -the isomerization of isoprene and the dimerization of cyclopentadiene. As is well known for diene syntheses, two reaction mechanisms are possible. A biradical mechanism in which the activated complex resembles an unsaturated hydrocarbon with an open bond, or a mechanism with a cyclic intermediate resembling the dimer.

The reactions were studied between the pressure range of 1 to several thousand atmospheres (whereby the reaction rate increases enormously with increasing pressure) and the following interesting results were obtained. In the dimerization of isoprene the volume of the activated complex is equal to the volume of the corresponding unsaturated hydrocarbon with an open bond, attesting to the biradical mechanism (Ch. Wholling and J. Peisakh). In the second reaction -the dimerization of cyclopentadiene- the volume of the activated complex is close to the volume of the reaction product -dicyclopentadiene. It was concluded that the latter reaction has a cyclic activated complex intermediate (B. Raistrick, R. Sapiro and D. Newitt, M. G. Gonikberg and L. V. Vereshchagin). Here the application of elevated pressures was extremely convenient for the study of activated complex structure.

In solution chemistry the reaction mechanism is usually solvent dependent. The medium effect on rate and reaction course is a cardinal problem of chemistry. Essentially, this involves the participation of the solvent in the transition state, or its effect on the properties of the activated complex. For instance, in all heterolytic reactions the activated complex is